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PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period January 1

to March 31, 1948, under Contract W-16-025-CWS-1318

By

J. C. Beesheer, F. A. Lenfesty, P. L. Tins, and G. W. Richardson

Wilson Dam, Alabama

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Tennessee Valley Authority
Division of Chemical Engineering
Wilson Dam, Alabama
April 7, 1948

Commanding Officer
Chemical Corps Technical Command
Building 330
Army Chemical Center, Maryland

Attention: Chief, Munitions Division

Gentlemen:

Transmitted herewith are six copies of the seventh quarterly progress report on our studies of phosphorus fillings for munitions. The report covers work performed under contract W-13-035-CWS-1318 during the period January 1 to March 31, 1948.

Very truly yours,

TENNESSEE VALLEY AUTHORITY

K. L. Elmore

K. L. Elmore, Chief
Chemical Research Division

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Progress Report on Work Performed in the Period January 1

to March 31, 1948, under Contract W-18-035-CWS-1518

SUMMARY

Results of calculations based on data obtained in thermal stability tests of experimental ~~phosphorus~~ fillings indicate that the stabilities of the fillings are about as high as can be expected from the properties of the materials comprising the fillings.)

(Conversions of white to red ~~phosphorus~~^P in 4.2 CM shells have been carried out. When the shells are quenched in water as soon as the conversion reaction is well under way, the conversion proceeds smoothly and safely to completion. The silver-soldered NRA shells will not stand the conditions imposed, 600°~~P~~^P ~~phosphorus~~^P ~~equivalent~~ at 560° C., when the shells are allowed to remain in the furnace throughout the conversion.)

P Ninety-six 4.2 CM shells have been filled with experimental phosphorus fillings. Of these, 2 were tested to destruction in the conversion of white phosphorus to massive red phosphorus. The other 94 shells have been sent to the Army Chemical Center for test.

- 666 -

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PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period January 1 to March 31, 1948, under Contract W-18-035-CWS-1818

In the 3-month period covered by this progress report, the experimental work was confined to determination of the proportions of the components of various fillings that would be expected to perform best in munitions. Five types of fillings comprising granulated white phosphorus and various binders were investigated. The binders were ordinary plaster of paris, plaster of paris set with an emulsion of white phosphorus in aqueous polyvinyl alcohol, Duralon, Thiolok LP-2, and Thiolok LP-2 modified with mercaptoethanol.

During a visit to the Army Chemical Center on October 13 to 17, 1947, it was agreed that TVA would charge some 4.2 CM shells with experimental fillings containing granulated white phosphorus and with red phosphorus prepared directly in the shells by conversion from white phosphorus. The present report describes the filling of 96 such shells, 94 of which have been shipped to the Center for evaluation.

PHYSICAL PROPERTIES OF FILLINGS

Effect of Water on Duralon and Thiolok LP-2 Fillings

It has been customary to dewater granulated phosphorus for use in Duralon fillings by blowing carbon dioxide downward through a column of the granules in a tube closed at the lower end by a porous plate. When the bulk of the water was displaced by the carbon dioxide, two successive portions of 95 per cent ethyl alcohol were poured over the granules and also displaced by a current of carbon dioxide. The purpose of the alcohol was to provide a substantially water-free mass of phosphorus granules and thus to obviate possible adverse effect of the water on the setting of the Duralon resin with which the granules were to be bound.

Granulated phosphorus for use in Thiolok LP-2 fillings was dewatered by washing with acetone in the same manner. The choice of solvent was based on compatibility with the binder, although only small amounts of the solvent were left on the phosphorus.

To determine the benefits derived from virtual dewatering of the granulated phosphorus with organic solvents, two series of Duralon fillings were prepared; in one series the phosphorus was washed with alcohol, and in the other the water clinging to the granules was not removed. Two similar series of Thiccol LP-2 fillings also were prepared, except that the drying agent was acetone.

With both fillings the use of granulated phosphorus wet with water made the initial mixtures of phosphorus and binder somewhat less fluid and more sticky, particularly towards metallic surfaces. This stiffening and tackifying of the mixtures, however, increased only to a small degree the difficulty of mixing and transferring the fillings. The water was without noticeable effect on the rate or extent of curing of either binder, or on the thermal stabilities of the cured fillings. It is concluded that washing of the phosphorus granules with alcohol or acetone will be neither necessary nor particularly desirable if these fillings are prepared on a large scale with mechanical equipment.

PVA Emulsion-Plaster of Paris Fillings

The tendency of emulsions of white phosphorus in aqueous polyvinyl alcohol, and of fillings prepared with these emulsions, plaster of paris, and granulated phosphorus, to occlude gas with concomitant increase in the volume occupied by the emulsion and the fillings has been reported previously. A further investigation was made of the apparent volumes occupied by known weights of several of these emulsion fillings. The emulsion contained 50 per cent by weight of emulsified white phosphorus and 50 per cent of a 4 per cent aqueous solution of medium-viscosity polyvinyl alcohol.

Each filling contained 173 grams of granulated phosphorus and 80 grams of the emulsion-plaster mixture. The fillings were placed in 8-ounce glass sample bottles and allowed to stand. The volumes of the fillings when freshly prepared and after standing for 24 hours were observed, and the results are listed in Table I. The increase in volume on standing apparently is due to release of occluded gas as the liquid phase of the emulsion is decreased by the setting of the plaster of paris. The gas so released probably would not result in the development of much pressure in a closed container. Relatively few gas pockets could be seen in the freshly prepared fillings, but after 24 hours, when the plaster of paris had set, numerous large gas pockets were visible. Although some of these fillings have stood up fairly well in short (3-hour) thermal stability tests, the presence of the large gas pockets makes it improbable that the fillings would remain ballistically stable on prolonged exposure to temperatures above the melting point of white phosphorus.

TABLE I

Apparent Volumes and Specific Gravities ofPVA Emulsion-Plaster of Paris Fillings

(Each filling contains 172 grams of granulated phosphorus
and 80 grams of emulsion-plaster binder)

Filling no.	1	3	5	7	2	4	6	8
Composition of binder, wt. %:								
Emulsion		77		74			69	
Plaster		23		26			31	
Apparent volume of filling, cc.:								
Fresh	160	165	160	160	165	165	165	170
24 hr.	158 ^a	165	160 ^a	170	165	190	180	180
Apparent specific gravity of filling:								
Fresh	1.58	1.53	1.62	1.60	1.53	1.53	1.53	1.48
24 hr.	1.63	1.56	1.56	1.48	1.53	1.53	1.40	1.40
Theoretical		1.70		1.72			1.74	

^a Includes 10 cc. supernatant free water.

Thermal Stability Tests

In evaluation of the thermal stability of experimental phosphorus fillings comprising granulated phosphorus and a solid binder, the location of the center of gravity, both along the longitudinal axis and laterally from that axis of a filled munition, is determined before and after heating the filled munition for 8 hours at 65° C. while lying on its side. The shift in the center of gravity of the entire munition or of the filling alone is a measure of the thermal instability of the filling and might be used to estimate the ballistic instability of the munition when fired from a weapon. On the other hand, the thermal stability of a filling that contains white phosphorus probably is expressed best in terms of the ability of the binder to retain the phosphorus at temperatures above the melting point of that element.

In the following discussion, the center of gravity of a munition or any of its components is located by its distance from the base of the munition as measured along a line parallel to the axis of the munition (longitudinal center of gravity), and its distance from the axis of the munition as measured along a line perpendicular to the axis (lateral center of gravity). The "torque" of a munition or any of its components is taken to mean the product of the weight of the munition or its component and the distance of the corresponding longitudinal center of gravity from the base of the munition.

Attempts were made to calculate, from the measured shift of the center of gravity, the amount of phosphorus that had run out of the body of the filling. Thermal stability tests in glass bottles had shown that the solid sponge formed by the binder, in which the granules of phosphorus were embedded, underwent no appreciable change. It was assumed that the shift in the center of gravity of the munition was due entirely to movement of phosphorus from the binder into the free space between the filling and the top of the munition. It was assumed also that the longitudinal center of gravity of the binder and the phosphorus it contained after the test was the same as that of the original filling, and that the phosphorus remaining in the filling was distributed uniformly along the axis of the filling, but not necessarily uniformly in a direction perpendicular to the axis.

From the weights of the fillings and the dimensions of the containers (M16 grenades and glass sample bottles) into which the fillings were charged for thermal stability tests, the volume occupied by the filling and the volume of free space between the filling and the top of the container could be calculated. The longitudinal center of gravity of the untested filling also could be calculated, as could the longitudinal center of gravity of any phosphorus that would run out of the filling in the thermal stability test and collect in the free space. With these data, the amount of phosphorus that was lost from the main body of the filling could be calculated in the following manner.

Since it is assumed that shift of the center of gravity of a munition during a thermal stability test is due entirely to the movement of phosphorus from the body of the filling to the free space between the filling and the top of the munition, the change in torque of the munition may be calculated either from the weight of the munition and its change in longitudinal center of gravity or from the weight of phosphorus that runs out of the filling into the free space and the difference between the longitudinal centers of gravity of the filling and the free space. When these two torques are equated, the weight of the phosphorus that runs out of the filling is the only unknown and can be determined readily.

Since the dimensions of the free space between the filling and the top of the munition are known, the lateral center of gravity of the volume occupied by the run-out phosphorus can be calculated, and in turn, the lateral unbalance due to the run-out phosphorus can be estimated.

The data on thermal stability tests of samples in glass sample bottles that were reported in Table IV of the progress report covering the period October 1 to December 31, 1947, were recalculated by the method described above. The results, together with some of the data presented in the earlier report, are shown in Table II of the present report. Although the agreement between the values "estimated" and the values "calculated" by the method outlined above is less close than is desirable, the general correlation between the two sets of values indicates that the method of calculation is sufficiently valid to show, at least roughly, the movement of phosphorus through and out of a solid binder of the type used in the TVA experimental fillings.

Data obtained from thermal stability tests of fillings in M15 grenades are shown in Table III. The plaster of paris fillings show consistently high thermal stability. Duralon and Thiokol LP-2 fillings appear to have practically the same thermal stability. The erratic behavior of the fillings prepared from polyvinyl alcohol emulsion and plaster of paris may be due to the fact that the L4 series was 14 days old when the tests were made, whereas the L5 and L6 series were only 7 days old.

Perhaps the most significant values in Table III are those in the last column, the percentage of the total unbalance calculated to be due to the phosphorus that had run out of the main body of the filling. In fillings bound with either ordinary plaster of paris or plaster of paris set with polyvinyl alcohol emulsion, about 33 per cent of the unbalance is due to the exuded phosphorus, but 80 per cent of the unbalance of the Duralon fillings, and 115 per cent of the unbalance of the Thiokol LP-2 fillings appears to be attributable to the exuded phosphorus. The value of 115 per cent for the Thiokol LP-2 fillings indicates that the calculations are somewhat inexact, but the relative values for each type of filling probably are in approximately the correct ratio to the values for the other types.

TABLE II

Thermal Stability Tests of Duralon and Thiokol LP-2Fillings in Glass Sample Bottles

Sample no.	Loss of WP, % ^a		Lateral unbalance of heated sample, gram cm.		
	Estd. ^b	Calcd. ^c	Measd. ^d	Estd. ^b	Calcd. ^c
<u>Duralon</u>					
E56	33.9	42.6	79.0	40.0	48.3
E80	35.9	27.7	53.5	46.1	41.4
E100	7.0	4.4	19.3	14.2	9.5
E120	3.4	4.2	13.9	7.0	8.9
<u>Thiokol LP-2</u>					
J30	16.0	9.8	32.8	29.0	19.2
J100	4.3	7.1	13.8	9.0	13.7
J120	2.3	3.7	13.8	4.9	7.8
<u>Thiokol LP-2 with Peroxyphenol</u>					
NEO	17.3	14.0	40.7	31.1	26.2
MI0C	11.1	5.5	14.0	20.7	11.1
MI2C	4.0	3.2	19.5	10.0	7.0

- ^a Per cent of total phosphorus charged that ran out of body of the filling.
- ^b Estimated from measurements, after solidification, of the phosphorus that had run out of the body of the filling.
- ^c Calculated from shift of center of gravity by method described in this report.
- ^d Direct measurement.

TABLE III

Thermal Stability Tests of Experimental Fillings in M15 Grenades

(Munitions heated 8 hours at 65° C.)

No.	Center of gravity, munition			Calculated movement of phosphorus	
	Initial long., ^a cm.	After test Long., ^a cm.	Lateral ^b , cm.	Run-out, % of charge ^c	Calculation due to run-out, % of mass ^d
<u>Duralon</u>					
E9A	5.96	6.10	0.079	7.1	60.2
E9B	5.96	6.08	0.071	6.1	58.0
E9C	5.95	6.02	0.013	3.5	214.2
E10A	5.95	5.99	0.022	2.0	80.8
E10B	6.11	6.22	0.056	5.7	70.1
E10C	6.00	6.13	0.032	6.7	70.4
E11A	5.97	6.12	0.036	7.1	73.4
E11B	6.00	6.13	0.033	6.3	69.2
E11C	5.95	6.07	0.018	6.1	66.0
E12A	6.08	6.21	0.033	6.5	70.8
E12B	6.12	6.23	0.037	5.7	75.1
E13A	6.14	6.23	0.032	4.6	66.0
E13B	6.16	6.22	0.036	3.1	60.5
<u>Phicol LP-2</u>					
J15A	5.93	6.05	0.044	6.0	100.0
J15B	5.95	6.09	0.043	7.1	106.6
J16A	6.06	6.10	0.035	2.0	49.7
J16B	5.96	6.11	0.031	7.5	155.6
J17A	6.06	6.16	0.031	5.2	126.2
J17B	5.97	6.01	0.022	2.0	79.7
J17C	6.06	6.14	0.013	4.1	214.2
J18A	5.97	6.04	0.031	3.5	38.0
J18B	5.95	6.10	0.048	7.5	99.1
J19A	6.02	6.10	0.031	4.1	98.8
J19B	5.95	6.03	0.027	5.5	151.2
J19C	5.97	6.08	0.039	5.5	100.7
J20A	6.06	6.16	0.039	5.6	103.6
J20B	6.00	6.18	0.027	1.8	60.1
J21A	6.05	6.19	0.040	7.1	123.1
J21B	6.08	6.16	0.027	4.1	115.3
J22A	6.09	6.21	0.032	6.1	133.1
J22B	6.08	6.21	0.031	6.8	138.0
J23A	6.05	6.21	0.037	8.2	143.6
J24A	6.12	6.25	0.027	6.9	156.0

TABLE XIX (Contd.)

No.	Center of gravity, munition			Calculated movement of phosphorus	
	Initial long., ^a cm.	After test Long., ^a cm.	Lateral ^b , cm.	Run-out, % of charge ^c	Unbalance due to run-out, % of measd. ^d
<u>Plaster of Paris</u>					
C12A	6.05	6.10	0.039	2.6	40.8
C12B	6.06	6.08	0.021	1.0	41.9
C12C	6.06	6.07	0.021	0.5	21.5
<u>Polyvinyl Alcohol Emulsion-Plaster of Paris</u>					
L4A	6.00	6.10	0.056	4.6	68.7
L4B	6.17	6.20	0.066	1.4	16.2
L4C	6.30	6.29	0.031	nil	nil
L4D	6.38	6.36	0.032	1.4	17.2
L5C	6.08	6.36	0.125	13.0	58.5
L5D	6.06	6.32	0.132	12.1	39.6
L6C	6.12	6.53	0.114	10.0	52.9
L6D	6.05	6.31	0.131	12.4	37.7

^a The longitudinal location of the center of gravity is measured from the base of the munition. The center of gravity of the empty M15 grenade with burster well in place varies fairly regularly and substantially linearly from 5.98 cm. for a 320-gram case and well to 7.22 cm. for a 345-gram case and well.

^b Movement of the center of gravity of the munition from the longitudinal axis. The centers of gravity of most filled grenades were on the longitudinal axes of the munitions; when the grenade was unbalanced initially, the lateral shift is the difference between the final and the initial positions.

^c Duralon, Thichol LP-3, and plaster of paris fillings each contained 253 grams of phosphorus. Fillings of polyvinyl alcohol emulsion and plaster of paris contained about 270 grams of phosphorus.

^d Lateral unbalance of phosphorus calculated to have run out of the body of the filling divided by the lateral unbalance found by measurement of the tested munition.

The porosity of plaster of paris, and particularly the large gas pockets of the emulsion-plaster fillings, probably permit settling of molten phosphorus through the bodies of these fillings, so that, with the munition on its side, the upper part of the body of the filling would be expected to contain less phosphorus than the lower part after a thermal stability test. The Duralon binder is a rigid material, and settling of phosphorus through this binder undoubtedly occurs, although to a less extent than in the plaster fillings. Thiokol LP-2 sets to an elastic rubbery solid, however, which presumably should expand somewhat under the pressure of molten phosphorus developed in the thermal stability tests. Because of the elasticity of this binder, ruptures in the walls of the cells in which the individual granules of phosphorus originally were contained might be expected to close up after enough phosphorus has been exuded to relieve the pressure, with the result that there should be less tendency for the phosphorus to settle downward through the body of the filling than there is in Duralon fillings in which ruptures of the cell walls probably are permanent.

The Duralon fillings exuded an average of 5.5 per cent of the phosphorus present, and the Thiokol LP-2 fillings exuded an average of 5.3 per cent. Data on the thermal coefficient of expansion of Thiokol LP-2 are not available. The manufacturers state that Duralon has about the same coefficient of expansion as steel, 12×10^{-6} per °C. Since the cubical coefficient of expansion is about 3 times the linear coefficient, a piece of Duralon, or the cavities in a sponge of Duralon, may be expected to increase to 1.0034 times the original volume on being heated 40° C. (from room temperature to 35° C., the temperature of the thermal stability test). Since solid white phosphorus at 25° C. has a specific gravity of 1.82, and molten phosphorus at 65° C. has a specific gravity of 1.725, the volume occupied by the phosphorus increases to 1.055 times its original size. If the solid phosphorus just filled the unheated sponge, then, assuming the sponge to be nonelastic,

$$(1.055 - 1.0034)/1.055 = 0.051,$$

or 5.1 per cent of the initial charge of phosphorus would be exuded from the body of the filling. The elastic Thiokol LP-2 apparently is more able to expand and thereby retain the molten phosphorus than is the rigidly solid Duralon, although the phosphorus remaining in Thiokol LP-2 fillings after thermal stability tests appears to be more uniformly distributed along planes perpendicular to the axis of the munition than the phosphorus remaining in Duralon fillings.

The fillings listed in Table III, particularly the Duralon and Thiokol LP-2 fillings, varied considerably in certain of their components. Attempts to determine the effect on thermal stability of such variables as particle size of the granulated phosphorus or modifications of the binder, as by addition of mercaptoethanol to Thiokol LP-2, were unsuccessful. Duplicate fillings often differed more between themselves than they differed from another filling containing the same binder.

It is concluded that the thermal stabilities shown in Table III, whether expressed as shift of the center of gravity or as the ability of the binder to retain molten phosphorus, reflect an inherent property of the binder. This property depends upon the porosity of a binder such as plaster of paris, and upon the coefficient of expansion of an impervious nonelastic binder such as Duralon. Since these characteristics are inherent in the binders, improvement of the thermal stability of fillings prepared with these binders may be accomplished only by modification of the properties of the particular binders, a method that does not appear to be feasible at present.

PREPARATION OF RED PHOSPHORUS IN 4.2 CM SHELLS

The 4.2 CM shells which were to be charged with massive red phosphorus, prepared by conversion of white phosphorus directly in the shell case, were filled with molten white phosphorus containing 1 per cent sulfur and practically free from water. The sulfur was added in the form of the 30-20 phosphorus sulfur eutectic. The burster wells were seated without application of lubricant or dope to the seat. Since the burster-well seat obviously is the weakest joint in the assembled shell, a threaded plug was screwed into the nose of the shell to press against the open end of the burster well and hold it securely in the seat. A hole was drilled through the threaded plug along its axis, and this hole was threaded at the top to receive a 1/4-inch standard pipe. The pipe served as a means of suspension of the shell and as a sheath for the thermocouple that was inserted into the burster well. The shell was heated in a vertical tube furnace that was supported above a 55-gallon drum about two-thirds full of water. The shell was suspended, by the pipe, from a cable running through a pulley above the furnace, so that the shell could be raised and lowered by remote control.

The shell containing the white phosphorus was heated in the furnace until the temperature indicated by the thermocouple in the burster well showed a marked increase in rate of rise. When this rapid rise of temperature indicated that the highly exothermic conversion had

started, the shell was lowered and completely submerged in the water. The pipe in the threaded plug extended above the water and kept the burster well dry. The temperature shown by the thermocouple in the burster well continued to rise for several minutes until a maximum was reached and maintained for a minute or so, after which the shell cooled fairly rapidly. When the shell had cooled to about 100° C., it was pulled up through the furnace and removed from the supporting nose plug.

Typical thermal histories of several shells are listed in Table IV. The rate of heating of the charges of white phosphorus in the shells apparently did not affect the temperature at which the conversion was initiated. The temperature at which the conversion was initiated varied from 240° to 290° C., as is shown in Table V. The maximum temperatures obtained in shells that were quenched in water as soon as the conversion was initiated varied from 415° to 539° C. These rather wide variations in observed temperatures probably are due as much to fortuitous differences in placement of the thermocouple in the burster well as to differences in the behavior of the various charges.

It will be noted that the conversion in shell R-16 in Table IV apparently was initiated at about 260° C., but that quenching of the shell stopped the reaction. This phenomenon, which has been observed a few times with charges in both M15 grenades and 4.2 CM shells, might complicate control of the large-scale production of phosphorus fillings by the general method employed here. It seems probable, however, that if the shells were permitted to attain a temperature of about 350° C. before being quenched, the conversion would always go to completion.

Three shells were left in the furnace after the conversion had been initiated. Only one, R-1 in Table IV, withstood the conditions imposed without noticeable leak.

Shells R-18 and R-23 (Table V) were left in the furnace until maximum temperatures of about 560° C. were reached; both of these shells developed bad leaks at the maximum temperature and were quenched immediately. Both shells increased in weight, as shown in Table V, presumably by intake of water through the failures that had permitted loss of phosphorus. An inspection of shell R-18 showed no apparent serious failure, but the base of shell R-23 was pushed almost out of its seat, and it is probable that, had this shell remained in the furnace, the base would have been blown completely out of the case. The M2A shell (silver soldered) apparently cannot stand the conversion without quenching; quenching cools the soldered joints enough to ensure sufficient strength to withstand the pressure generated in the conversion.

TABLE IV

Thermal Histories of Conversions of White to
Red Phosphorus in 4.2 CM Shells

Shell R-12			Shell R-13			Shell R-16			Shell R-1		
Time, Temp., °C.			Time, Temp., °C.			Time, Temp., °C.			Time, Temp., °C.		
min. ^a	Fce. ^b	Shell ^c	min. ^a	Fce. ^b	Shell ^c	min. ^a	Fce. ^b	Shell ^c	min. ^a	Fce. ^b	Shell ^c
15	61	8	0	388	39	0	345	12	0	383	0
30	110	14	15	315	85	15	536	46	15	369	72
45	157	27	30	333	140	30	354	113	30	356	138
60	195	43	45	357	209	45	377	177	45	351	190
75	223	78	60	380	261	55	393	219	60	364	227
90	261	109	61	-	263	56	-	224	70	-	251
105	289	144	62	-	267	57	-	228	71	-	253
120	313	172	63	-	271	58	-	231	72	-	255
135	343	221	63.5 ^d	26	276	59	-	236	73	-	256
150	368	264	64	28	283	60	402	239	74	-	257
151	-	267	65	32	342	61	-	242	75	-	268
152	-	269	66	34	423	62 ^d	41	257	76	-	343
153	-	272	67	36	487	63	44	302	77	-	366
154	-	275	68	37	513	64	47	315	78	-	512
155	-	280	69	38	513	65 ^f	400	310	79	-	534
156 ^d	8	305	70	39	497	65.5 ^g	-	324	80	-	547
157	11	443	71	39	473	66	50	367	81	-	555
158	14	497	72	40	449	67	51	416	82	-	560
159	16	519	75	41	373	68	52	433	83	-	562
160	17	529	80	42	392	69	53	429	84	-	563
161	19	531	85	42	181	70	53	415	85	384	564
162	20	521	90 ^e	42	125	71	54	398	86	-	565
163	21	504				72	54	381	87	-	565
164	22	483				75	55	326	88	-	562
165	22	462				80	55	240	89	-	558
170	24	336				85	55	172	90	-	552
175	25	186				90 ^e	55	124	95	394	522
185 ^e	26	80							100	389	497
									105	384	474
									110	377	453
									115 ^d	0	435
									120	-	374
									125	-	241
									130	-	137
									135 ^e	5	70

^a Measured from time shell was placed in furnace.

^b Temperature of furnace tube while shell is in furnace and of water in quenching tank after shell is quenched, or external temperature to which shell is subjected.

^c Temperature indicated by thermocouple in burster well.

^d Shell lowered into water.

^e Shell removed from water.

^f Shell raised from water back into furnace.

^g Shell lowered again into water.

TABLE V

Conversion of White to Red Phosphorus in 4.2 CM Shells

No.	Empty ^a	Shell weight, grams		Weight of WP charge, grams	Temperature, °C.	
		Initial	Converted		Start of conversion	Maximum
R-1	6695	10265	10270	3570	260	565 ^c
R-2	6665	10150	10155	3465	240	415
R-3	6675	10135	10140	3460	240	408
R-4	6685	10235	10225	3550	250	427
R-5	6670	10255	10250	3500	250	451
R-6	6665	10170	10170	3505	275	507
R-7	6605	10205	10205	3520	250	-
R-8	6605	10030	10035	3375	270	475
R-9 ^b	6655	10200	10190	3545	255	437
R-10 ^b	6690	10080	10080	3390	255	433
R-11 ^b	6665	10185	10185	3520	270	478
R-12	6675	10110	10115	3435	280	531
R-13	6670	10155	10160	3485	275	518
R-14	6655	10195	10200	3540	285	539
R-15	6670	10155	10150	3435	270	520
R-16	6620	10245	10245	3525	250+	433+
R-17	6635	10140	10140	3505	290	536
R-18	6645	10155	10160	3510	275	556 ^c
R-19	6665	10065	10065	3320	255	517
R-20	6670	10135	10135	3765	Leaked badly at 190°	
R-21	6645	10140	lost	3795	Burst at 220°	
R-22	6650	10185	10145	3485	260	483
R-23	6645	10145	10210	3500	280	532 ^c
R-22	6690	10070	3565	3480	245	465

^a Weight, to nearest 5 grams, of shell, burster well, and plastic nose cap.

^b Initial charge contained 75% WP, 25% RP.

^c Remained in furnace during conversion.

Shell R-M2 (Table V) was the only welded shell in which the white-to-red conversion was carried out. This shell smoked badly before the conversion was initiated, and the tabulated data show that the shell lost at least 100 grams of phosphorus. An inspection of the quenched shell showed that most of the leak was through the joint between the adapter and the nose of the case, although some leakage also had occurred at the joint between the base and the case.

In shells R-1 to R-11 and shell R-M2 in Table V, the catalyst was not well mixed with the charge, but in shells R-12 to R-23 the charge was thoroughly mixed by shaking the freshly charged shell while the phosphorus was still molten. The somewhat lower temperatures at which the conversion was initiated in the first group of shells may well be due to high local concentrations of catalyst, for it has been found, in conversions of white to red phosphorus in M16 grenades, that increase in the amount of sulfur tends to lower the temperature of initiation of the conversion.

Shells R-9, R-10, and R-11 were charged with a mixture of about 75 per cent white and 25 per cent red phosphorus. As shown in Table V, these charges behaved almost exactly like those containing only white phosphorus. Since the red phosphorus in the initial charge did not lower the maximum temperature obtained in the conversion, the use of red phosphorus in the initial charge does not seem to be of any advantage.

Shells R-20 and R-21 inadvertently were filled with excessive charges of white phosphorus. Shell R-21 began to smoke at about 215° C., and when the temperature reached 220° C., the base of the shell was pushed entirely out of the case by the expansion of the phosphorus. There was a mild explosion, which raised the shell about 2 feet, but most of the phosphorus fell into the quenching tank. Shell R-20 began to smoke profusely at 190° C., whereupon it was quenched and discarded. The usual charge of white phosphorus, 3500 grams, amounts to 1.52 grams per cc. of free space in the 4.2 CM shell (2310 cc.). Charges of as large as 1.55 gram of WP per cc. (Shell R-5) have been subjected to the conversion, but the 1.64 grams of WP per cc. in shells R-20 and R-21 obviously is greater than the capacity of the fairly inelastic container. The maximum permissible charge probably is close to 1.55 grams of WP per cc. of volume in the shell.

An attempt was made to estimate the heat of reaction in a number of conversions. A small quenching tank with a capacity of about 40 liters was provided with a pump to circulate the water. The temperature of the water was measured with a 10-junction iron-constantan thermocouple. A measure of the correction to be applied for the heat

content of the shell before conversion was made by quenching two shells before conversion was initiated. The results of the measurements, listed in Table VI, are less consistent than is desirable, but they are close to the value of 16.0 kg.-cal. per mole of P_4 that is reported in the literature. Shells R-12, R-13, and R-16 in Table IV were three of those used in the determination of the heat of reaction. The uncorrected rise of the temperature of the water in the quenching tank is reported in Table IV. Because the weight of the shell was nearly twice the weight of the charge of phosphorus, the correction for the heat in the shell before conversion began was about as large as the heat of the reaction.

TABLE VI
Heat of Reaction in the Conversion of White
to Red Phosphorus in 4.2 CM Shells

Shell no.	Temperature, °C.		Heat of reaction, kg.-cal. per mole of P_4
	Start of conversion	Maximum	
R-12	255	517	15.0
R-13	275	518	16.2
R-16	250+	433+	16.9
R-22	260	483	17.2
R-16	270	520	17.5

EXPERIMENTAL FILLINGS CONTAINING GRANULATED WHITE
PHOSPHORUS IN 4.2 CM SHELLS

In addition to the 24 shells in Table V that were filled with massive red phosphorus, 72 other 4.2 CM shells were filled with experimental fillings comprising granulated white phosphorus and a binder. These shells have been sent to the Army Chemical Center for test. Six different fillings were made, and 12 shells were charged with each filling. Descriptions of these fillings are given in Table VII.

TABLE VII

Experimental Phosphorus Fillings in 4.2 CM Shells Submitted
For Test at Army Chemical Center

Plaster of Paris, designated "C"

Binder, parts by weight:	plaster of paris	100
	water	100

Plaster of Paris, designated "D"

Binder, parts by weight:	plaster of paris	100
	water	100

PPA Emulsion-Plaster of Paris, designated "I"

Binder, parts by weight:	50% emulsion of WP in 4% aqueous solution of polyvinyl alcohol, medium viscosity	70
	plaster of paris	25

Duralon, designated "E"

Binder, parts by weight:	Duralon 30	100
	Activator F	7.2
	Activator G	2.0

Thiokol LP-2, designated "J"

Binder, parts by weight:	Thiokol LP-2	100
	furfural	20
	formic acid	4

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-17-

TABLE VII (Contd.)

Thiokol LP-2 with Mercaptoethanol, designated "M"

Binder, parts by weight:	Thiokol LP-2	100
	furfural	20
	formic acid	4
	mercaptoethanol	1

Type designation	Particle size of granulated WP, wt. %		Weight, grams		
	-4 +8 mesh	-8 mesh	Gran. WP	Binder	Total
C	40	60	2254	1130	3374
D	0	100	2205	1130	3335
L	30	70	2050	950	3000
E	40	60	2205	966	3171
J	30	70	2205	957	3162
K	30	70	2205	957	3162

The granulated phosphorus used in fillings "C", "D", and "L" were dewatered only by blowing carbon dioxide through the column of phosphorus in the drying tube. The granulated phosphorus used in filling "E" was washed with alcohol, and that used in fillings "J" and "K" was washed with acetone.

The weights of the fillings listed in Table VII are those used in the preparation of the mixture for each shell. The granulated phosphorus was weighed under water before drying; the variable hold-up of liquid by the granules and the mechanical losses entailed in the loading operation resulted in variations in the weights of the fillings placed in the individual shells. With the exception of the fillings in the "C" series, the phosphorus for which was not carefully dried, variations from the total weights given in Table VII were less than 100 grams.

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-18-

REVIEW OF RESULTS AND PLANS FOR TERMINATION OF CONTRACT

It has been shown that massive red phosphorus fillings may be prepared in 4.2 CM shells by heating charges of white phosphorus in the shells to some temperature, between 250° and 300° C., at which the exothermic conversion reaction is initiated, and quenching the shell in water when the reaction is well under way. The quenching appears to be necessary because the maximum temperature of about 550° C. that may be reached is high enough to soften the silver solder used in the M2A shell sufficiently to permit failure of the nose or base joints under the pressure generated in the conversion unless the joints are cooled. The case itself apparently can withstand the pressure generated when the shell is not quenched, and modification of the shell to provide joints that will remain gastight under an internal pressure of 800 pounds per square inch at 550° C. would expedite large-scale application of the conversion. The shells then could be passed through a furnace maintained at some temperature between 300° and 350° C. and removed at any time after completion of the conversion. If the shells are to be quenched, however, any device that would ensure quenching of each shell when a temperature of about 550° C. is attained in the burner wall probably would permit large-scale use of this method in preparing massive red phosphorus fillings in 4.2 CM shells and similar munitions.

The filling of ninety-six 4.2 CM shells with experimental charges for tests at the Army Chemical Center completed substantially all the experimental work under this contract. A summary report covering all the work performed under the contract will be prepared and submitted to the Army Chemical Center by April 30, 1948, on which date the contract is to be terminated.

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